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(21) International Application Number: PCT/GB97/00774 (22) International Filing Date: 20 March 1997 (20.03.97) (30) Priority Data: 9605911.8 21 March 1996 (21.03.96) GB (71) Applicant (for all designated States except US): RAYCHEM LIMITED [GB/GB]; Faraday Road, Dorcan, Swindon, Wiltshire SN3 5HH (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): PERCY, Michael, John [GB/GB]; 88 Hallsfield, Cricklade, Wiltshire SN6 6LS (GB). BRENAC, Luc [FR/FR]; 11, rue Guillaume-Tell, F-17017 Paris (FR). GANSBUEHLER, George [GB/GB]; 4 Harptree Close, Nine Elms, Shaw, Swindon, Wiltshire SN5 9UN (GB). (74) Agents: JAY, Anthony, William et al.; Raychem Limited, IPLD, Faraday Road, Dorcan, Swindon, Wiltshire SN3 5HH (GB).		(81) Designated States: AU, BR, CA, CN, CZ, HU, JP, KR, MX, NO, PL, RU, TR, US, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: GEL CARRYING ELONGATE ARTICLES (57) Abstract Articles comprising a tube of plastics material extruded over or co-extruded with an interior lining of filling of gel are useful <i>inter alia</i> for sealing electrical connections. The tube may be crimpable and may enclose metal crimp connectors. Preferred gel sealants include block copolymers having a highly oil-extended alkylene elastomeric mid-block and harder styrene or alkyl methacrylate end blocks.		

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GEL CARRYING ELONGATE ARTICLES

This invention relates to elongate articles carrying gel which may find many uses, for example in sealing and protecting elongate objects such as electrical wiring connections.

The invention provides an article comprising an tube of plastics material extruded over or co-extruded with an interior lining or filling of gel. The gel may line or fill the tube over substantially its entire length, or may line or fill it only partially or at intervals along its length. The gel may also line the tube substantially completely around or only partly around its inner perimeter, and fillings of the gel may fill the tubular cross-section substantially completely or only partly, usually more than halfway.

The shape of the tube is not critical, square or hexagonal profiles, for example, being feasible, and the same applies to the tubular profile of the gel linings, the internal surfaces of which may, but need not, follow the same profile as the said tube. For many purposes it may be preferable that the tube has a rounded, more preferably a substantially circular, cross-sectional shape, which is also the preferred form for the tubular linings of gel.

A resiliently-flexible tube may have advantages for some purposes. However, less flexible, and especially crimpable, tube materials are preferred for certain purposes hereinafter described. The plastics material of the tube may accordingly be selected from extrudable thermoplastics, elastomers, thermoplastic elastomers, and other materials to suit the intended end use of the gel-containing articles. The articles according to this invention may be especially useful, for example, when the polymeric material of the tube is selected to be substantially permanently deformable by mechanical crimping, preferred tube materials for this purpose including polyolefines, especially high-density polyethylene. In such cases, the gel filling or lining will preferably be of sufficient volume to seal the tube after crimping, and a portion of the gel may exude from the tube as a result.

Another preferred form of article according to the present invention has one or more metallic crimp connectors aligned within the tube. These metallic crimps may be introduced by any convenient method, preferably by feeding them sequentially with, or into, the gel as it is being extruded, preferably as it is being co-extruded into the tube. Thus, the crimps may be forced into the already-extruded body of gel, or may be fed to

the gel extrusion head (suitably modified if necessary) with the gel material. This provides a desirably economical continuous process for forming gel-filled crimps in which the gel is capable of sealing the crimp connections made by the crimp connectors in use.

In preferred articles according to this invention, the gel and the tube material have been co-extruded in a molten state, and preferably under elevated internal and external pressure, to enhance the adhesion of the gel to the tube, perhaps tending to form an intermingled or enhanced-contact bondline interface. It is preferred that the adhesion strength of the gel material to the tube is greater than its adhesion strength to a body with which it is to be placed in sealing contact in use. Usually, it will be preferable for the cohesive strength of the gel to exceed its adhesion strength, at least to the tube and body used in specific cases, and especially to itself.

Alternatively, the gel, especially if of a relatively firm consistency capable of forming a self-supporting tubular profile, may be pre-formed as a tube or solid profile and the tube may then be extruded over it, for example using known kinds of apparatus and techniques used for extruding polymer insulation onto electrical wires. Good adhesion may still be obtained, for example by pre-heating the gel and/or by selecting suitably compatible materials for the tube and the gel. Primers and/or bonding agents may also be used to enhance adhesion.

The invention accordingly includes a preferred method of forming an article according to this invention, comprising co-extrusion of the said tube and the said gel both in a molten state and cooling to solidify the resulting tube and its gel lining or filling. Also included is the alternative method of first extruding the gel and subsequently extruding the tube onto the pre-formed gel, preferably after warming the gel surface. Suitable processing equipment and conditions will readily be selected by those familiar with such extrusion technology.

Compatible materials to achieve desirably high levels of adhesion may be selected by trial and error. Preferred materials for at least the inner surface region (preferably for the whole) of the tube in some cases include materials composed of, or comprising as a majority component, ethylene/vinyl acetate copolymer containing less than 40%, preferably less than 20%, by weight of vinyl acetate, ethylene/alkyl (preferably methyl) acrylate copolymer containing less than 40%, preferably less than 20%, by weight of alkylacrylate, or polyethylene, preferably high-density polyethylene for crimpable tubes. Alternatively, for more resiliently-flexible tubes, elastomer materials, preferably thermoplastic elastomer materials, especially olefinic elastomers, are desirable, examples

of which include very low density polyethylene (VLDPE) plastomer, e.g. Dow Plastics' Engage CL8001 (Trade Mark), which is believed to be a polyolefin elastomer of ethylene with 25% octene co-monomer; polyether/polyester block copolymer, e.g. DuPont's Hytrel (Trade Mark) softer, lower-melt-viscosity grades such as G4074; and polypropylene-based elastomer, e.g. DSM's Sarlink 3140 (Trade Mark), which is believed to be a polypropylene/EPDM blend having a Shore A hardness (5 seconds) of 42 (extruded) to 49 (injection moulded).

Especially good compatibility and adhesion between the tube and the gel may be achievable by making the tube out of the same or closely related polymers as the preferred triblock gels, but without the gel-forming high content of extender liquid for the mid-block. Triblock copolymers of the kinds mentioned herein may be compounded with known fillers and other ingredients to form tube materials which will tend to have useful affinity to the same or similar polymers forming the gel.

As previously mentioned, the gel material is preferably a thermoplastic gel, although crosslinked or thermoset gels are not excluded. It is preferred that the gel has substantially elastic deformation up to an elongation of at least 100%; and that the gel has ultimate tensile strength (ASTM D412) less than 1 MPa, dynamic storage modulus less than 50 kPa, and substantially zero slump at temperatures up to 100°C, preferably up to 120°C.

In an especially preferred form of article according to this invention, the gel material is an oil-extended hard block-elastomeric block-hard block triblock copolymer, preferably one in which the hard end blocks comprise polystyrene or a polymethacrylate, and/or preferably one in which the elastomeric mid-block comprises a hydrogenated or unhydrogenated polyalkylene, preferably polybutadiene, polyisoprene, or more preferably polyethylene/butylene and/or polyethylene/propylene. Most preferred are gels comprising (i) a styrene-alkylene block copolymer, preferably a styrene- (hydrogenated alkylene)-styrene triblock copolymer, more preferably a styrene-(ethylene/propylene and/or ethylene/butylene)-styrene triblock copolymer having a weight average molecular weight M_w of at least 180,000, and (ii) at least 300 (preferably at least 400, more preferably at least 500) parts by weight of extender liquid per 100 parts of the block copolymer, which liquid extends and softens the alkylene blocks of copolymer.

Preferred gels made from styrene-(ethylene/butylene)-styrene (SEBS) block copolymers, and test methods for defining and characterising these and other gels are

described in WO-A-8800603 (RK308) and WO-A-9005166 (RK403), the disclosures of which are incorporated herein by reference. The most-preferred gels described in WO-A-9323472 (RK469), the disclosure of which is incorporated herein by reference, are made from styrene-(ethylene/propylene)-styrene (SEPS) block copolymers, in which the ethylene/propylene mid-block may include some ethylene/butylene units. These preferred SEPS copolymers have weight average molecular weight M_w of at least 180,000, preferably at least 200,000, more preferably at least 220,000, and polystyrene content of 25-45 weight percent, preferably 28-40 weight percent, more preferably 29-36 weight percent, and are made with substantially or wholly non-aromatic extender liquid. The gels are preferably soft, high-temperature-slump-resistant, springy gel compositions, by which is meant liquid-extended polymer compositions having an ultimate elongation (measured by ASTM D412 modified as described below) greater than 100%, with substantially elastic deformation (i.e. substantially no hysteresis) to an elongation of at least 100%; ultimate tensile strength (ASTM D412) less than 1 MegaPascal; dynamic storage modulus less than 50,000 Pascals; and substantially zero slump at temperatures up to 100°C, preferably up to 120°C, more preferably up to 135°C, and especially up to 150°C.

The invention for some purposes may be more particularly concerned with such gel compositions comprising 2-40 weight % of the styrene-alkylene-styrene triblock copolymers based on the weight of the whole composition, preferably those comprising from 4% to 35%, especially 4 to 25%, by weight, of the triblock copolymer and at least 500 parts by weight of extender liquid per 100 parts by weight of the gelling polymer, in which the said copolymer comprises more than 50%, preferably more than 75%, more preferably more than 90%, and especially more than 95%, by weight, or substantially all, of the total gelling polymer present. Various additives may be present, for example the tackifiers described in WO-A-9005166 or the polyphenylene oxide described in WO-A-8800603, or styrene-alkylene di-block copolymers, e.g. styrene-ethylene/propylene or styrene-ethylene/butylene diblock copolymers, for reducing the loss of extender liquid as described in WO-A-9305113 (RK451), the disclosures of all of which are incorporated herein by reference.

Specific embodiments of the invention will now be described by way of example, with reference to the accompanying drawing showing schematically a series of metal crimp connectors 10 being fed through a hollow extruder pin 12 into a gel extrusion stream 14 as it is co-extruded with a surrounding thermoplastic tube extrusion stream 16. The finished article leaving the extruder head comprises the crimps 10 enclosed in a gel lining within the co-extruded thermoplastics tube. Depending on the extrusion pressures

and temperatures used, the gel may be caused to flow into the space 18 between the crimp connectors and into the connectors themselves to fill them partially or completely with gel.

The relative diameters and wall thicknesses of the tube and the gel are not critical, and may be selected to suit specific end uses. It may be desirable in many cases to use a gel lining whose radial thickness is less than 0.5 times, preferably less than 0.25 times the tube inner radial dimension. For circular tubes and gel linings, in other words, the thickness of the tubular gel lining may usefully be less than one third, preferably less than one sixth, of the internal radius of the tube. The gel lining wall thickness will preferably be not less (often considerably greater) than the tube wall thickness, but thinner layers of gel may be useful in some circumstances. Variations from, and within, these preferred ranges of radii and/or wall thicknesses may be selected to suit particular requirements. Overall tube diameters ranging from a few millimetres to a few centimetres, preferably 0.25 cm to 3 cm, especially 0.5 cm to 2 cm, are likely to be useful in most cases. For avoidance of doubt, the terms "tube" and "tubular" as used herein are to be understood as including any elongate hollow body resembling a pipe or conduit, regardless of its cross-sectional shape.

Typical gels might have a Voland hardness of 60 gms (11.5% Septon (Trade Mark) 2006 and 4.5% Septon 1001 with remainder non-aromatic oil); or Voland hardness of 100 gm (14% Septon 2006 and 8% Septon 1001 with remainder non-aromatic oil). Typical tube materials might be Sarlink (Trade Mark) thermoplastic elastomer of Shore hardness 40, 60 or 80, or Thermolast (Trade Mark) thermoplastic elastomer of Shore A hardness 25.

Another useful form of article according to the present invention, derived from those hereinbefore described, is one whose tubular length is less than its largest outer diameter, preferably less than half, more preferably less than one quarter, of its largest outer diameter. Such articles may be regarded as rings (usually substantially circular, although other configurations are not excluded), which may have been formed by cutting from a longer length of the tubular article. Other methods of making such relatively short tubes or rings may be envisaged, but cutting from longer lengths is usually more convenient in practice. The expression "largest outer diameter" is intended to include shapes other than substantially circular.

These ring-like articles may advantageously be put to use as a gasket between opposed pressure surfaces, or as a grommet on an elongate object (e.g. a wire) passing through the article, especially where it is desired to seal a larger aperture through which the elongate member also passes, which aperture fits closely around the perimeter of the grommet provided by the ring-like article. It may be preferable for such rings to have a lining of gel rather than being completely filled with the gel.

In most forms of the various aspects of this invention, it will be preferable that the tube is substantially continuous and substantially free of voids (meaning unintended voids).

Especially preferred articles according to the various aspects of this invention are those wherein the gel comprises a thermoplastic triblock copolymer having a fluid-extended elastomeric mid-block and having end blocks (preferably polystyrene or polymethacrylate end blocks) which are substantially impervious to the extender liquid of the mid-block, and the tube is of plastics material, for example comprising ethylene/vinylacetate copolymer as a majority by weight of the polymer content. The triblock copolymer gels will preferably have the characteristics and meet the criteria described in any or all of EP-A-0426658 (RK308), WO-A-9305113 (RK451), WO-A-9323472 (RK469), and WO-A-9418273 (RK472), the disclosures of all of which are incorporated herein by reference. Those disclosures deal mainly or wholly with triblocks having polystyrene end blocks. For higher temperature performance, it may be preferable to use the new triblock gels having polyalkylmethacrylate end blocks described in WO-A-9700292 (RK509).

A further aspect of the present invention provides an article comprising a shaped body of gel, preferably the triblock gels hereinbefore described, a surface region of which has been chemically-modified to alter its chemical resistance or other properties over substantially all of its exterior surface or that part thereof which will be exposed in use to environments which would otherwise unacceptably affect the body of gel. Such articles may resemble the extruded tube articles hereinbefore described if the surface modification is applied to an elongate (for example extruded) body of gel to form a skin thereon, for example by cross-linking a surface layer of the gel by electron beam or UV radiation after

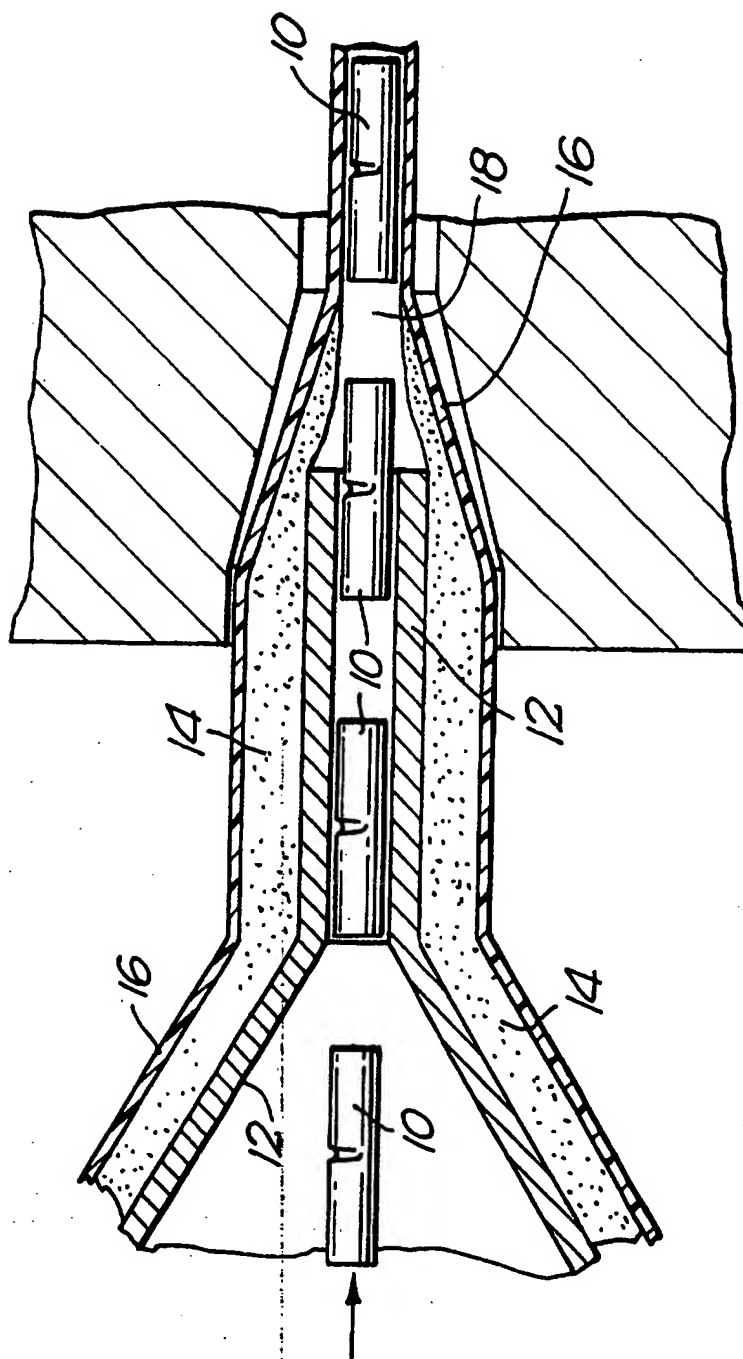
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treating it with suitable cross-linking agents (known per se). The modified surface skin may be extremely thin, leaving the softness and conformability of the gel substantially unimpaired while improving its chemical resistance, for example to solvents or petrol (gasolene) or other fluids with which it may come into contact in use, e.g. as a gasket or seal. The use of a modified surface region for such purposes, according to this aspect of the present invention, is to be distinguished from skin formation on gels merely to reduce their surface tack and/or improve their physical handling or strength characteristics.

CLAIMS:

1. An article comprising a tube of plastics material extruded over or co-extruded with an interior lining or filling of gel.
2. An article according to claim 1, wherein the polymeric material of the tube is selected to be substantially permanently deformable by mechanical crimping.
3. An article according to claim 1 or 2, wherein the tube is formed of polyolefin, preferably high-density polyethylene.
4. An article according to any preceding claim, having one or more metallic crimp connectors aligned within the said tube.
5. An article according to any preceding claim, wherein the gel material is an oil-extended hard block-elastomeric block-hard block triblock copolymer, preferably one in which the hard end blocks comprise polystyrene or a polymethacrylate, and/or preferably one in which the elastomeric mid-block comprises a hydrogenated or unhydrogenated polyalkylene, preferably polybutadiene, polyisoprene, or more preferably polyethylene/butylene and/or polyethylene/propylene.
6. A method of making an article according to any preceding claim, comprising co-extrusion of the said tube and the said gel both in a molten state and cooling to solidify the resulting tube and its gel lining or filling.
7. A method of making an article according to any of claims 1 to 5, comprising first extruding the gel and subsequently extruding the tube onto the pre-formed gel, preferably after warming the gel surface.
8. An article comprising a shaped body of gel, a surface region of which has been chemically-modified to alter its chemical resistance or other properties over substantially all of its exterior surface or that part thereof which will be exposed in use to environments which would otherwise unacceptably affect the body of gel.

9. An article according to claim 8, comprising an elongate tube or solid body of the gel on which the modified surface region corresponds to the outer tube of an article according to any of claims 1 to 5.
10. A method of forming an article according to claim 8 or 9, comprising providing the said body of gel with cross-linking agents in at least the said surface region and cross-linking the said surface region by UV or electron beam radiation.



INTERNATIONAL SEARCH REPORT

Int. .onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01R13/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 140 746 A (DEBBAUT CHRISTIAN A M) 25 August 1992 see abstract; claims; figures ---	1,2,4,6, 9,10
A	EP 0 108 518 A (RAYCHEM CORP) 16 May 1984 see abstract; figures 7,8 see page 1-8 ---	1-4,6,9, 10
A	WO 92 14278 A (RAYCHEM LTD ;RAYCHEM SA NV (FR)) 20 August 1992 see abstract; claims; figures ---	1-4,6,9, 10
A	WO 94 18273 A (RAYCHEM LTD ;HAMMOND PHILIP JAMES (GB); HUDSON JOHN MICHAEL (GB);) 18 August 1994 cited in the application see the whole document ---	5-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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